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THE EFFECTS OF PHOTOCHEMICAL REACTION SUBSTANCES ON PLANTS

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THE EFFECTS OF PHOTOCHEMICAL REACTION SUBSTANCES ON PLANTS
[Kōkagaku hannō busshitsu no shokubutsu ni oyobosu eikyō]

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Among the photochemical substances which are air pollutants, those which are known to have a strong toxicity towards plants include ozone, PAN, and nitrogen dioxide. Even though ozone is the main one of the photochemical substances, there still appears to be argument concerning the percentage it occupies among them. In California, 90% to 95% of the photochemical substances are ozone, while the rest consists of PAN and others. Therefore, ozone is regarded as being the main cause of plant damage and is the pollutant which is given the greatest importance.

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In our country the problem has become serious only quite recently, but it has been said that the percentage occupied by ozone has a low value which is quite different from that of California. The existence of a type of smog peculiar to Japan alone is apparently being considered as a real possibility. Little is known as yet about the composition of the photochemical substances in various sections of Japan. However, from the standpoint of the symptoms displayed by the damaged plants, in many cases the characteristics are obviously those connected with ozone, and it is believed that, in Japan as well, it will still be necessary to give primary consideration to the effects of ozone when one is considering the harmful effects caused by photochemical substances.

In view of the preceding, let us first of all outline the historical background and the present situation concerning the occurrence of plant damage in our country.

I. Plant Damage Believed Caused by Photochemical Substances in Our Country

Public attention came to be focused on damages caused by photochemical substances since the summer of 1970, when there were effects on the human organism in Tokyo as well as the occurrence of spots and of abnormal leaf fall in the zelkova trees. Since then, damages caused by photochemical substances have come to be noted throughout the country, chiefly in the larger cities. However, the occurrence of damage to farm produce believed to be caused by ozone can be dated back even earlier than this. Suspicions of ozone damage were first entertained concerning tobacco plants. The group of Kunisawa et al.

[1-5] made detailed studies concerning the physiological spot disease in tobacco plants and established that this disease occurred widely in 1965 in the Inland Sea area around Osaka, Okayama, and Takamatsu, and that it also occurred to a considerable degree in the Kanto area as well beginning around 1966. The usual characteristics are white spots, but brown spots are also said to occur. There is an intimate connection between the occurrence of these spots and the ozone concentration in the atmosphere. When the concentration rose above 8 - 9 pphm (0.08 - 0.09 ppm), there was an increased frequency of occurrence, and there was 100% occurrence at concentrations above 11 pphm. They report that the symptoms are also similar to those of ozone damages and that the same symptoms could be obtained with reproduction tests.

Since the tobacco plant is one of the types of plants which are most susceptible to ozone (there are, to be sure, differences depending on the variety, and Bel-W3 is the most susceptible of all) and tends to display easily the typical signs of ozone damage, it is believed that this is what led to the discovery of ozone damage. Recently, however, damages believed to be caused by ozone have occurred, not only in tobacco plants, but in many other types of farm crops, and problems have occurred especially in the various sections of the Inland Sea area. For example, a disease in the taro which is tentatively called "white splash disease" can be reproduced experimentally after two hours of contact with 0.4 ppm of ozone. Various other symptoms occurring in the taro, such as brown splashes or intercostal withering, are also suspected to be caused by ozone damage. Damages believed to be caused

chiefly by ozone have occurred also in onions, daikon radishes, and spinach. It has also been reported by Sawada et al. [6] that smog damages have occurred within the Tokyo metropolitan area in various types of vegetables such as onions, Chinese cabbage, and rape seedlings. The same types of damages have been reported also in Chiba prefecture by Matsuoka et al. [7].

The whitish withering of the tips of onion leaves does not appear to be confined solely to conditions caused by ozone alone. However, this phenomenon has recently been conspicuous throughout the country. This is true not only of our country. Similar phenomena invited comment quite a long time ago in the United States. The earliest report there was in 1903, when Whotzel reported whitish withering of the tips of onion leaves in Wisconsin. Microscopic examination reportedly did not reveal the presence of any bacteria or fungi. Many studies were carried on subsequently, and for a period of 15 years it has been impossible to confirm the presence of any sort of pathogenic microorganisms. The common conditions for the occurrence of this disease are the following. First, it occurs after the rainy season during periods of strong sunlight, high temperature, and low humidity. Second, the rate of incidence differs for different varieties of onions. Third, it is not caused by excessive or insufficient nutriments. When Engle et al. [8] fumigated various varieties of onions for two hours with 0.4 ppm of ozone and inspected them 48 hours later, they found as a result that the same symptoms of white withering of 2 - 3 cm at the tips of the leaves were obtained. It was also possible to reduce

the damages by sprinkling with carbamate type agricultural chemicals, which are said to be "antiozonants." On the basis of these results, they doubt whether the withering of the tips of the onion leaves is a damage caused by ozone.

However, oxidant damages in various types of plants began to appear in clear form in 1944, when Middleton found a heterogeneous disease in the alfalfa and other plants in Los Angeles. This has been even more so since 1952, when it was established that this was caused by atmospheric pollutants based on photochemical reactions. Since then, as damages of this type have intensified, they have come increasingly into the limelight. However, it is assumed that, even without the conditions of photochemical smog existing at the present day, ozone damages must have existed in the past as well, and Heggestad [9] holds that it will be necessary to elucidate the photochemical reactions with nitrogen dioxide and carbohydrates coming from the vegetation and soil in farm areas. In particular, he says that it will be necessary to clarify the reasons why the maximum ozone concentration was 0.91 ppm in those regions of Wisconsin where the tips of the onion leaves withered.

Strong ultraviolet rays are necessary in order for photochemical substances to occur, and it is universally known that far-reaching damages have been inflicted in California, where there is little rainfall and much strong sunshine. However, plant damages are not necessarily confined only to areas with these types of meteorological conditions. For example, according to Mukammal [10], tobacco spot disease occurs widely on the Canadian north shore of Lake Erie; he reports that this is caused by ozone. This fact indicates that

even in our country, where the meteorological conditions differ greatly from those of the Los Angeles region, sufficient attention must be paid to plant damage caused by photochemical substances.

II. Various Effects on Plants

As was mentioned before, the symptoms of damage differ greatly depending on the varieties of the damaged plants. However, there are, furthermore, great differences in the symptoms of damage within the same variety depending upon the conditions. As is true of other gases as well, this is so because the reactions differ depending upon the concentration -- that is, the damages may be acute or chronic. However, one of the remarkable characteristics of ozone is the very fact that the symptoms of damage are so very diverse. In the following let us describe the conditions under which damages may occur and the symptoms with reference to each separate component.

1. Ozone

In acute damages, the damage symptoms may be classified as follows for different types of plants and within the same type. (1) Reddening of the leaves (tends to occur in grapes, sorrel, etc.). (2) Bleaching of the upper surfaces of the leaves. (3) Small, white, freckle-like spots (grapes, tobacco, tomato, etc.). (4) Dark brown dot-like spots (citrus fruits, avocado, etc.). (5) Massive necrosis (generally tends to occur easily when damage is severe). (6) Ring-shaped spots of yellow to yellow-brown color (pine, etc.). (7) Chlorosis. The most distinctive of these symptoms are the small, white, freckle-like spots

as shown in Fig. 1. Another characteristic of ozone, according to Koukol et al. [11], is reddening, that is, the appearance of anthocyanin pigments.

Fig. 1.

As for the small spots, they appear on the upper surfaces and not on the lower surfaces of the leaves in the broadleaf trees in spite of the fact that stomata are not present on the upper surfaces of the leaves. According to Taylor [12], this can be explained by the following. That is, ozone is obviously absorbed through the stomata on the lower surfaces, but much is absorbed in the palisade parenchyma which abounds in chlorophyll. Consequently, it has been reported by Hill et al. [13] that damages occur to the same extent on both the back and the front surfaces in plants which have no differentiation between the palisade parenchyma and the spongy parenchyma. In the pine, yellow to yellow-brown ring-shaped spots appear midway down the needles. However, the chronic symptoms caused actually by smog damages are observed to be the following. That is, browning occurs gradually starting from the bases of the needles, and leaf fall is accelerated. In onions,

small spots occur initially at the tips of the leaves, and the tips of the leaves later turn white and wither.

As for the degree of susceptibility, there are many reports. The results of Ledbetter et al. [14] concerning the patterns of the damages which appear and the susceptibility are as shown in Table 1.

Table 1

Comparison of ozone susceptibility of various types of plants (Ledbetter)

1 植物	種類	2 感受性	3 症状のタイプ		
			モザイク	点状斑点	小斑点
7 トマト	Lycopersicum esculentum MILL. var. Bonny Best	×××?	++		
8 ビーン	Phaseolus vulgaris L. var. Pinto	×××	+	+	
9 タバコ	Nicotiana tabacum L. var. Maryland Mammoth	×××	++		
10 ホーレンソウ	Spinacia oleracea L. var. Early Hybrid 7	×××	++		
11 ポテト	Solanum tuberosum L.	×××	++		
12 ヤナギタデ	Perennial Polgonum sp.	×××			++
13 タバコ	Nicotiana tabacum L. var. Vamors 48	××			++
14 コリウス	Coleus blumei BENTH.	××	+.	+	
15 キク	Chrysanthemum sp. var Pippin	××	+	+	
16 アルファルファ	Medicago sativa L.	××	++		
17 ピーナツ	Arachis hypogaea L.	××	+		+
18 タバコ	Nicotiana tabacum L. var. Turkish	××	+		++
19 カンシ	Ipomoea batatas LAM. var. Porto Rico	×	+		+
20 オジギソウ	Mimosa pudica L.	×	++		
21 ブドウ	Vitis sp. vars. ZING, Tokay, Concord	×		++	
22 ビジョザクラ	Verbena sp. var. L. A.	×	++		
23 キク	Chrysanthemum sp.	×		++	
24 アボカド	Persea sp.	×		++	
25 テンサイ	Beta vulgaris L.	×	+		++
26 イチゴ	Fragaria sp. var. Empire	×		++	
27 ペッパーミント	Mentha piperita L.	×		+	
28 ゼラニウム	Geranium sp.	×	+		
29 グラジオラス	Gladiolus sp. var. Snow Princess	0			
30 ペポ	Capsicum frutescens L. var. Grossum Bailey	0			
31 ビーン	Phaseolus vulgaris L. var. Tendergreen	0			

32 (1) 各植物とも多数品種を含み、感受性は変動する。
×××：0.1ppm以下で激しく発現、××：0.1～0.3ppmで激しく発現、×：0.3～1.0ppmで発現、0：1.0ppmで発現なし、++：激しくその傾向が強い、+：ときどきその傾向が発現。

[Key on next page]

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Key to Table 1:

1. Type
2. Susceptibility
3. Type of symptoms
4. Necrosis
5. Dot-like spots
6. Small spots
7. Tomato
8. Bean
9. Tobacco
10. Spinach
11. Potato
12. Smartweed
13. Tobacco
14. Coleus
15. Chrysanthemum
16. Alfalfa
17. Peanut
18. Tobacco
19. Sweet potato
20. Mimosa
21. Grape
22. Verbena
23. Chrysanthemum
24. Avocado
25. Sugar beet
26. Strawberry
27. Mint
28. Geranium
29. Gladiolus
30. Pepper
31. Bean
32. (Note): Each plant was fumigated for 8 hours. Judgments were determined by visible symptoms.
    xxx: damages occurred at less than 0.1 ppm
    xx: damages occurred at 0.1 - 0.3 ppm
    x: damages occurred at 0.3 - 1.0 ppm
    0: no damages at 1.0 ppm
    ++: symptoms occurred always
    +: symptoms occurred sometimes

Besides, Heggestad [9] adopted the following classification, supplementing the results of Middleton and Taylor.

Most susceptible types (genera):

Avena (oats), Lycoperisicum (tomato), Nicotiana (tobacco), Phaseolus (kidney bean), Pinus (pine), Poa (poa grass), Polygonum (jointweed), Solanum (eggplant), Spinacea (spinach). Visible damages appear in 2 hours at 0.10 ppm, in 4 hours at 0.08 ppm, and in 8 hours at 0.05 ppm.

Least susceptible types (genera):

Capsicum (pepper), Gladiolus (gladiolus), Kalanchoe (kalanchoe), Tolmiea. Visible damages appear after more than 8 hours at 1.0 ppm.

Plants with little resistance are useful as index plants. For example, Bel-W3 tobacco is used, at least in the United States, as an index plant in Connecticut, New York, New Jersey, Delaware, Pennsylvania, Maryland, South Carolina, Florida, Ohio, Utah, California, and other states. Citrus fruits have a great resistance, and continuous exposure for 10 days is required at 0.4 ppm before visible damages will appear. However, the citrus fruits of southern California are remarkably weakened by ozone even when visible damages do not appear, and it is said that lemon growers have been caused damages of $533 per acre. Grapes are more susceptible than citrus fruits. Richards et al. [15, 16] record intense visible damage caused by ozone, also in southern California. In the same area, Thompson et al. [17] ventilated Zinfandel grapes for 14 weeks with filtered air and unfiltered air (maximum concentration

during this period 0.25 ppm). As a result, the chlorophyl content in the unfiltered air plot was 28.8 $\mu g/cm^2$, but that in the filtered air plot was 48.8 $\mu g/cm^2$. The yield in the unfiltered air plot was 1,669 g, and that in the filtered plot was 1,892 g. Although there were little differences in the acid contents of the fruits, there was a difference of approximately 20% in the sugar contents between both plots. The report stated as a result that the oxidants have a big influence on the yield and the quality of grapes. As for trees, Kadoda [18] showed that deciduous broadleaf trees are somewhat less vulnerable than herbaceous plants and that evergreen broadleaf trees tend to be the least susceptible of all, as is shown in Table 2.

Table 2.

Degree of ozone damage in various trees (Kadoda)

Type	Degree of damage on mature leaves
Poplar	+++
Plane	$\pm \sim +$
Weeping willow	$\pm \sim +$
Cork oak (Q. variabilis Blume)	$\pm \sim +++$
Japanese oak (Q. serrata Thunb.)	$\pm \sim ++$
Japanese bush clover (Lespedeza bicolor)	+++
Keyaki (Zelkova)	$- \sim +$
Japanese privet	-
Eurya japonica	-

[Continued on next page]

Table 2 [continued from p. 11]

Type	Degree of damage on mature leaves
Oleander	-
Camphor tree	-
Torabe	± ~ +

Treated with 0.2 ppm ozone for 3 ~ 5 hours.

Temperature: 24.5 ~ 28°C

-: No damage

±: Less than 10% of leaf area

+: 10 - 30%

++: 30 - 50%

+++: More than 50%

Not only are there differences between different types in their resistance, but even within a single plant there are positions where damages tend to occur easily and those where they do not. With ozone, damages do not occur easily in immature leaves and old leaves; leaves immediately after maturation, when productive metabolism is most active, are most easily attacked. In this respect, ozone resembles sulfurous acid gas and nitrogen dioxide, although ozone must naturally have its own unique mechanism. Dugger et al. [19] review in detail the mechanism of the effects of oxidants on plants; they hold that the radiant energy during growth is an important factor in the differences in susceptibility at different leaf ages. The presence of rays of light is necessary for

the occurrence of ozone damage, but the effects of the light rays are not a simple matter of opening up the stomata, which in turn causes an increase in the absorption of gas, therefore increasing the damage. In this respect, the situation bears a resemblance to the results of measurements made by the writer [20] concerning sulfurous acid gas. There are many reports about the relationship between the degree of opening of the stomata and ozone damages. Some hold that there is a positive relationship between the degree of opening of the stomata and the degree of the damage, but most hold that there is no relationship. As for the functions of the stomata with respect to gas exchange, there is a hyperbolic relationship in agricultural crops, and there is a high gas exchange ability even when the stomata gap is very small. Even though the aforementioned relationship between the damage and the presence of light rays or the differences in resistance between different types may be explicable to a certain degree in terms of the degree of opening of the stomata, it would be difficult to use this to explain all the other phenomena. However, Dugger et al., basing themselves on the relationship between the state of stress of the moisture in the body and the damage, held that the causal factors for the resistance were located in the roots rather than in the leaves. However, in this sense, it would not be possible to ignore the effects of the stomata entirely, and it is probable that they have an indirect influence.

No doubt the damage mechanism is a complex one and is not governed by any one factor alone. The following phenomena have also been recognized. That is, it has been observed that there is increased

respiration preceding visual damages. Dugger et al. [21] fumigated young lemon trees weekly with 15 - 25 pphm for eight hours a day, five days a week. As a result, visual damages appeared after 7 - 10 weeks. However, it was found that respiration in the ozone plot had already begun to increase after the first week, as is shown in Fig. 2, and that by the fourth week there was an increased respiration amounting to 70 ml/fresh weight in comparison with the control. In connection with this, the sugar contents in the body underwent changes as shown in Table 3, and there was a pronounced decrease in the starch contents. Even though there were no changes in the sucrose, there was a big increase in the reducing sugar. They suppose that the reason for this is either that ozone inhibits the synthesis of starch from hexose or that it accelerates the hydrolysis of starch.

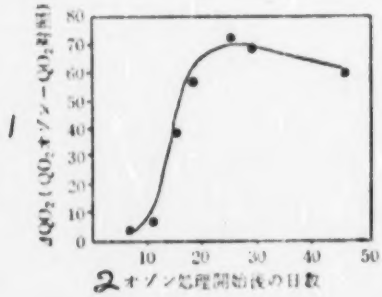

Fig. 2. Effects of ozone on respiration of lemon leaves (Dugger et al.) (O_3 : g/fresh weight/hr)

Key: 1. ΔQO_2 (QO_2 ozone - QO_2 control)
2. Number of days after commencement of ozone treatment

Table 3

Sugar contents of lemon leaves treated with ozone (Dugger et al.)

Treatment	Reducing sugar	Cane sugar mg/g fresh weight	Starch
Control	1.3 ±0	7.4 ±0.1	46.6 ±1.2
Ozone	5.2 ±0.4	7.8 ±0.2	28.8 ±0.7

Furthermore, ozone destroys the semipermeability of the protoplasmic membrane and increases the permeability. It is said that this occurs because the double bond of the unsaturated fatty acids in the protoplasmic membrane is destroyed. The increase in the permeability precedes the increase in respiration, but this phenomenon occurs during the initial stage of the effects of ozone. The fact that this is so is proved by the fact that there is an increase in the plants' ability to absorb ^{14}C-sugar from their leaves. In addition, it is said that ozone prevents the formation of new lipids by destroying the sulfhydryl group.

Concerning the histological changes, Thompson et al. [22] treated pinto beans for ½ - 24 hours with ozone of 0.6 - 1.0 ppm and then examined them with the electron microscope. The first change they discovered as a result was that granules had been formed and were arranged inside the stroma of the chloroplast (the stroma being a substrate containing lamellae and consisting chiefly of hydrophilic protein). The second change they observed was the destruction of the protoplasmic membrane and the tendency for the cell contents to assemble at the center of the cell. Chloroplast generally has similar properties,

namely the formation of osmiophilic granules when exposed to osmium. However, information is still lacking about the relationships between these granules and about the connections between the above-mentioned changes in the components and the histological changes. No doubt the pathways of these mechanisms will differ depending upon the ozone concentration, and consequently it is quite possible that the damages may be divided up into various types depending upon the appearances they assume when they appear.

If the mechanism of the damages could be clarified to a certain degree, it would be possible to make use of it in finding ways to lessen the damages. However, at the present moment we have not yet reached the point where actual application is possible. Theoretically speaking, there are two stages. That is, at the first stage, at the moment when the ozone arrives at the surface of the leaves, it would be sufficient to decompose it, to cause it to be absorbed by some substance, or else to impede its absorption into the leaves. At the second stage, it would be sufficient to administer physiological activity to the plant body and to detoxicate inside the body any ozone which had been absorbed. As a first method for this, Jones [23] held that spraying the leaf surfaces with activated charcoal or iron oxide was effective, and Kunisawa et al., whom we have already mentioned, also recognize the effectiveness of activated charcoal. When Thompson et al. [24] applied DPPD(N N'-diphenyl-p-phenylated iamine), which is a wax for storing oranges, three times to grapes, it was effective, he reports, with a high degree of significance. As for the second method, Freebairn et

al. [25] report that vitamin C and reduced glutathione were effective. It has also been said that carbamate type bactericides are effective. These are said to have been effective against withering of tips of onion leaves, as mentioned above.

However, it would be difficult in actual practice to apply these chemicals at all times, although it would probably be possible to reduce the damages by applying them from time to time, in the sense that the chronic damages caused by the cumulative effects of the gas might be reduced.

The main point in growing plants is to enable the plant body to grow up in health, and careful attention ought to be paid to imbalance in fertilization.

Brewer et al. [26] report that when large amounts of nitrogen were used in mangels and spinach the damage was increased, and that the damage was reduced only when all three elements were given.

2. PAN

These are said to have eye irritant properties with respect to the human organism, but with respect to plants they have approximately the same toxicity as ozone. However, since the amounts present in the atmosphere are small, they alone have little danger of causing damage. PPN (peroxy-propionyl nitrate) and PBN (peroxy-butyryl nitrate) are also said to belong to this family. They have a toxicity 4 - 8 times stronger than PAN. However, their amounts present in the atmosphere are small, and in particular PBN is said to be present in minute quantities

only in heavily polluted atmospheres. Therefore, it is believed that these are pollutants which will present no problems at all in actual practice.

The visible damages caused by PAN are characteristic. The initial symptoms involve merely the appearance of some small spots of the oil immersion type. However, when the degree of damages increases, the lower surfaces of the leaves will become silvery gray and glossy. When the damages advance further, pinto beans will turn brown, and necrosis will appear even on the upper surfaces of the leaves. The reason why the leaves turn a silvery gray color is said to be because the tissues in the vicinity of the stomata are attacked, causing voids there. The positions where the damages appear are also diametrically different from those in ozone damage. Immature leaves tend to be attacked selectively, and mature leaves have little susceptibility. When young leaves have undergone a certain amount of damage, their subsequent growth will deteriorate, the leaves will become small in size, or there will be deformities, as shown in Fig. 3. The differences in the tendencies for damages to occur at different leaf ages are as shown in Fig. 4, according to Dugger et al. [19]. It is also clear that in both ozone and PAN there is no relationship between the degree of the damages and the degree of opening of the stomata.

Fig. 3.

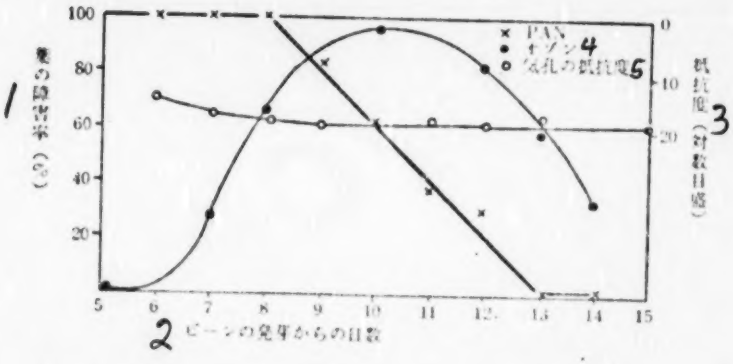

Fig. 4. Relationships between percentage of damages by ozone and PAN, leaf age, and degree of opening of stomata (Dugger et al.)
(Opening of stomata is expressed as resistivity registered on the bolometer)

Key:
1. Percentage of damaged leaves (%)
2. Number of days after germination of beans
3. Resistivity (logarithmic scale)
4. Ozone
5. Resistivity of stomata

It is not yet clear what effects on growth are exerted by low-concentration gases unaccompanied by any visible damages. It is said that the apparent photosynthesis, measured from the absorption ratio of carbonic acid gas, is not affected unless visible damages appear in the leaves. According to Taylor [12], there is a sudden decline in photosynthesis immediately before the appearance of visible damages.

According to Taylor [27], actual plant damages caused by PAN have been observed in at least 19 states in the United States; the biggest economic losses are said to be those in California. According to him, the concentrations which have been measured in California include values of 20 - 30 ppb at Riverside, where a maximum concentration of 58 ppb has continued for two hours. In Los Angeles, a high value of 210 ppb has been measured. In the most susceptible types of plants, plant damage (visible damages) will occur after four hours of exposure to 14 ppb. The writer himself has observed with pinto beans than when the concentration reaches 200 ppb intenses damages such as those illustrated in the figure above will occur in 40 - 60 minutes. Therefore, with values such as those measured in the examples mentioned above, there is a high degree of danger that damages caused by PAN will occur.

The differences in resistance of different types of plants are, according to Taylor and MacLean [28], as shown in Table 4. The mechanisms of the relevant damages and the changes in the electron microscopic tissue findings are similar to those which occur in the case of ozone, but the factors determining the differences in the

positions where the damages occur are as yet unclear.

Table 4

Resistance of plants to PAN (Taylor & MacLean)

1 弱い 植物			
2 ビントビーン	Phaseolus vulgaris L.	9 イラクサ(小麦)	Urtica ureans, L.
3 ヨダンソウ	Beta chilensis. Hort.	10 オ ー ト	Avena sativa, L.
4 ハ コ ベ	Stellaria media, Cyill	11 ペチュニア	Petunia hybrida, Vilm.
5 ダ リ ア	Dahlia, sp.	12 トマト	Lycopersicum esculium, Mill.
6 ブルーグラス	Poa annua, Linn.		
7 レ タ ス	Lactuca sativa, L.		
8 カラシナ	Brassica juncea, Coss.		
13 中 程 度			
14 アルファルファ	Medicago sativa, L.	20 ギシギシ	Rumex crispus, L.
15 オオムギ	Hordeum vulgare, L.	21 アカザ	Chenopodium album, L.
16 テンサイ	Beta vulgaris, L.	22 ソラマメ	Glycine max, Merr.
17 テーブルビート	Beta vulgaris, L.	23 ホウレンソウ	Spinacea oleracea, L.
18 ニンジン	Daucus carota, L.	24 タバコ	Nicotiana tabacum, L.
19 ゼニアオイ	Malva parviplora L.	25 コムギ	Triticum sativum, Lam.
26 強い 植 物			
27 アザレア	Rhododendron, sp.	34 キュウリ	Cucumis sativus, L.
28 ライマビーン	Phaseolus limensis, L.	35 タマネギ	Allium cepa, L.
29 ベゴニア	Begonia, sp.	36 ツルニチニチソウ	Vinca, sp.
30 ブロッコリ	Brassica oleracea, L.	37 ハツカダイコン	Raphanus sativus, L.
31 キク	Chrysanthemum, sp.	38 モロコシ	Sorghum vulgare, Pers.
32 トウモロコシ	Zea mays, L.	39 ホウセンカ	Impatiens, sp.
33 ワタ	Gossypium hirsutum, L.		

Key:
1. More susceptible types
2. Pinto bean
3. Beet
4. Chickweed
5. Dahlia
6. Blue grass
7. Lettuce
8. Mustard plant
9. Nettle
10. Oats
11. Petunia
12. Tomato
13. Medium degree
14. Alfalfa

[Key continued on next page]

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15. Barley
16. Sugar beet
17. Table beet
18. Carrot
19. Mallow
20. Sorrel
21. Goosefoot
22. Broad bean
23. Spinach
24. Tobacco
25. Wheat
26. Less susceptible types
27. Azalea
28. Lima bean
29. Begonia
30. Broccoli
31. Chrysanthemum
32. Corn
33. Cotton
34. Cucumber
35. Onion
36. Periwinkle
37. Radish
38. Sorghum
39. Balsam

3. Nitrogen Dioxide

Among the nitrogen oxides, this has the greatest toxicity against plants. However, it has a lower toxicity than other pollutants, amounting to about one-tenth that of sulfurous oxide gas. There are few research reports concerning it, largely because its concentration in the atmosphere has not been high thus far. However, since nitrogen oxides are produced together with the combustion of organic matter, as consumption of petroleum fuels increases, more careful attention will be necessary because this may cause the formation of ozone and PAN, as described above.

Table 5

Resistance of plants to nitrogen dioxide (Taylor & MacLean)

1 強い植物			
2 アザレア	Rhododendron, sp.	7 カラシナ	Brassica, sp., L.
3 ピントビーン	Phaseolus vulgaris, L.	8 ヒマワリ	Helianthus annuns, L.
4 カユプテ	Melaleuca leucadendra	9 タバコ	Nicotiana glutinosa, L.
5 ヒビスカス	Hibiscus rosasinensis		
6 レタス	Lactuca sativa, L.		
10 中程度			
11 ゼニアオイ	Malva parviflora, L.	14 ブルーグラス	Poa annua, L.
12 ヨコベ	Stellaria media, Cyrill	15 オレンジ	Citrus sinensis, Osbeck
13 タンポポ	Taraxacum officinal, Weber	16 ライムギ	Secale cereale, L.
17 弱い植物			
18 アスパラガス	Asparagus officinalis, L.	23 エリカ	Erica, sp.
19 インゲンマメ	Phaseolus vulgaris, L.	24 イクソラ	Ixora, sp.
20 カリッサ	Carissa carandas	25 アカザ類	Chenopodium, sp.
21 コロトン	Coltactum, sp.		
22 ケンタッキーブルーグラス	Poa pratensis, L.		

Key:
1. More susceptible types
2. Azalea
3. Pinto bean
4. Cayupte
5. Hibiscus
6. Lettuce
7. Mustard plant
8. Sunflower
9. Tobacco
10. Medium degree
11. Mallow
12. Chickweed
13. Dandelion
14. Blue grass
15. Orange
16. Rye
17. Less susceptible types
18. Asparagus
19. Kidney bean
20. Carissa
21. Croton
22. Kentucky blue grass
23. Erica
24. Ixora
25. Chenopods

The differences in resistance of various types of plants are, according to Taylor and MacLean [28], as shown in Table 5. According to VanHaut et al. [29], the types with little resistance are apples, pears, larch, rusan , red clover, tobacco, carrots, lupine, barley, and the sweet pea. Those with medium-degree resistance are tomatoes, celery, wheat, petunias, and dahlias. Those with great resistance are the locust tree, the ginkgo, the beech, the hornbeam, cabbage, onions, and the gladiolus. As for the concentration at which visible damages appear, according to Middleton et al., in the pinto bean it is 3 ppm for 4 - 8 hours. The writer also has observed that damages occur in pinto beans and tomatoes at concentrations of 10 ppm or more within 40 - 60 minutes. The citrus plants have a great resistance. According to MacLean et al. [30], after fumigation for four hours with a concentration of 50 ppm, leaf fall of about 50% will be observed, as is shown in Fig. 5.

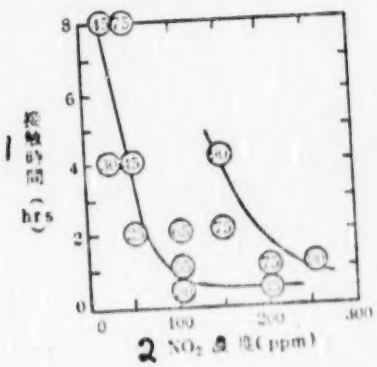

Fig. 5. Leaf fall of young citrus leaves after exposure to high concentrations of NO_2 (Numbers enclosed within circles are the mean leaf fall ratios of six types of citrus plants, MacLean et al.)

Key: 1. Duration of period of exposure (hrs)
2. NO_2 concentration (ppm)

However, Bush et al. state that in tobacco chlorosis occurred with low gas concentrations such as those which are observed in the atmosphere around Los Angeles (about 0.5 ppm, maximum 3.93 ppm). Taylor et al. [31] also reported that in pinto beans and tomatoes there was a significant drop in growth and an intensification of the green coloring when they were treated at 0.5 ppm for 10 - 22 days. In the author's unpublished experiments it was also observed that visible damages did not appear in the fruits of the summer bitter orange even at quite high concentrations, and also that there was a higher content of amino acids synthesized from $^{14}CO_2$ as compared with those treated with sulfurous acid gas.

Fig. 6.

The characteristics of the visual damages, as shown in Fig. 6, are quite similar to those of sulfurous acid gas, with necrosis between veins tending to occur easily in the mature leaves. Even though the symptoms of damage are the same as those in sulfurous acid gas damage, the mechanisms are believed to be entirely different in both cases, as will be described below.

III. Indirect and Composite Damage

Indirect damage may also be called a sort of composite damage. However, this is the type of phenomenon in which a pollutant will act as the attractive cause inducing parasitism of pathogenic bacteria or insect pests. Attention in this respect is being given to increased withering of pines caused by insect pests. These relationships have been demonstrated clearly by the reports of Stark et al. [32] and others. As is shown in Table 6, when the Ponderosa pine has been weakened to a certain degree by oxidants, there will be increased parasitism by insect pests.

Table 6

Oxidant damage in Ponderosa pine and its relationship to insect pest parasitism (Stark et al.)

Degree of chlorosis[a]	Percentage of trees with parasites		
	Western pine beetle[b]	Mountain pine beetle[c]	Trees attacked by other types
Healthy (0 - 1)	22.2 %	0 %	13.5 %
Medium (2 - 4)	19.1	13.6	30.4
Severe (5 or more)	58.7	86.4	56.1

a) 0: healthy, ... 9: very severe

b) Dendroctonus brevicomis LeConte.

c) D. ponderosae (Hodkins)

The reason for this is that oxidants cause physiological changes in the trees. It is indicated that the decreases in the discharge pressure of the resin and in the amounts of resin discharged, as well as the

qualitative changes causing the resin to be more easily crystallized, facilitate parasitism by insect pests. They also state that the decrease in the moisture contents in the bark part probably has some influence on the presence of insect pests. Since it is not easy to prove causal relationships for this type of damages, there are many as yet unknown areas. At the present time, withering caused by pine weevils has become conspicuous in our country as well, and it will probably be necessary to conduct thorough observations concerning the sort of relationships mentioned above.

Next, with respect to composite damage, this is generally attributed to the action of two or more gases. When they are compounded, there are some cases when they display the so-called synergistic effect, in which their effects are strengthened by the presence of other gases, while in other cases the effects are simply additive. Problems are presented in particular by the synergistic effect, generally in cases when ozone and sulfurous acid gas are combined. As an actual example, Applegate et al. [33] describe the synergistic effect in an area polluted with sulfurous acid gas which was combined with ozone produced by lightning, affecting peanuts. They reported that a synergistic effect occurred experimentally as well when 3 pphm of ozone and 15 pphm of sulfurous acid gas were used. The same thing has also been proven experimentally by Menser et al. [34]. However, these phenomena characteristically occur within a definite range of concentration. According to Heggestad [9], the synergistic effect occurs in tobacco when the ozone concentration is 0.03 ppm and the sulfurous acid gas

concentration is within the range of 0.1 - 0.3 ppm. According to a report of the Washington Air Pollution Bureau [35], when the sulfurous acid gas concentration is 0.05 - 0.25 ppm, a synergistic effect will be displayed if ozone is also present. On the other hand, Tingey et al. [36] fumigated radishes for five weeks, at a rate of 40 hours a week, with ozone and sulfurous acid gas at concentrations of 0.5 pphm each but were unable to observe any synergistic effect either in the growth or in the yield. In the author's own experiments [37] as well, in the pinto bean when concentrations of each gas which would cause only extremely slight damages if used alone were combined together, a synergistic effect would be displayed; when concentrations which would cause damages of medium degree or greater if used alone were combined, the effect was additive. To summarize these results, the following explanation ought to be adopted. That is, in order for both gases to display a synergistic effect, the criterion is not the absolute concentration. Rather, the synergistic effect is displayed as a result of mixing of gases which, if used alone, would be at the subliminal concentration level for generation of visual damages. The synergistic effect, furthermore, does not appear readily in the case of chronic damages or intense damages.

Sulfurous acid gas and nitrogen dioxide also display a synergistic effect. Typical results obtained by the writer [37] for various types of crops, evaluated on the basis of acute damages, are shown in Table 7; there is clearly a synergistic effect. Even when the gases are not mixed, if they both are used alternately, there will be observed an

orientation in their sequence of operation. When nitrogen dioxide was used after sulfurous acid gas, the damages were so great as to resemble the synergistic effect, but the damages were light in the opposite direction. Study is necessary about whether this phenomenon can be observed also in the case of chronic damages or not. However, the results indicate that both gases, which are extremely similar in the characteristics of their damages and in the positions where the damages occur, have different mechanisms of operation.

Table 7

Effects on tomatoes when treated with NO_2 or SO_2, when treated with NO_2-SO_2 mixtures, and when alternately treated with both

	/ 葉位の被害率（本葉で位置）					
	1	2	3	4	5	6
2 NO_2 13ppm 30分＋30分	0.3	8.8	17.8	17.8	5.5	0
3 SO_2 2.3ppm 30分＋30分	0.3	2.8	10.3	17.0	5.0	0
4 NO_2・30分＋SO_2・30分	0	1.8	3.0	3.3	0.3	0
5 SO_2・30分＋NO_2・30分	2.0	16.5	53.8	67.5	15.0	10.3
6 混 合 30分＋30分	65.0	85.0	78.8	32.5	1.0	0

Key: 1. Percentage of area damaged (in leaf order on major leaves)
2. NO_2 13 ppm 30 min. + 30 min.
3. SO_2 2.3 ppm 30 min. + 30 min.
4. NO_2 · 30 min. + SO_2 · 30 min.
5. SO_2 · 30 min. + NO_2 · 30 min.
6. Mixture 30 min. + 30 min.

Mixture of ozone and hydrogen fluoride does not have a synergistic effect. According to Brewer [38], no synergistic effect could be observed when lemons were treated with 2 ppb of hydrogen fluoride and 0.25 ppm of ozone.

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